

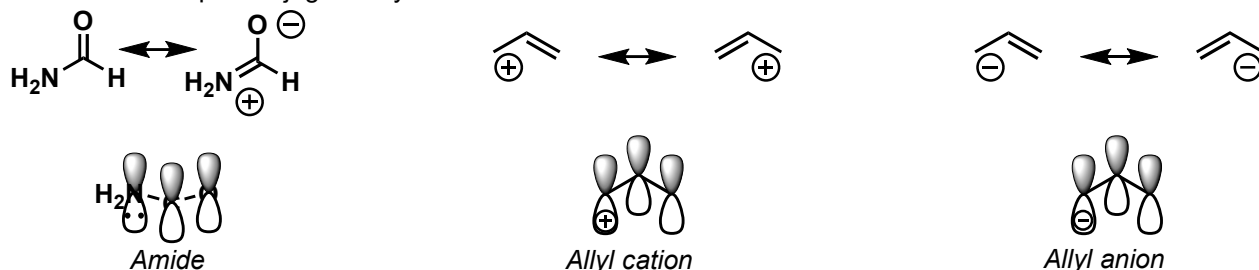
## Chemistry 17: Section Handout 4

Topics: Conjugation, Hückel MO Theory, Aromaticity

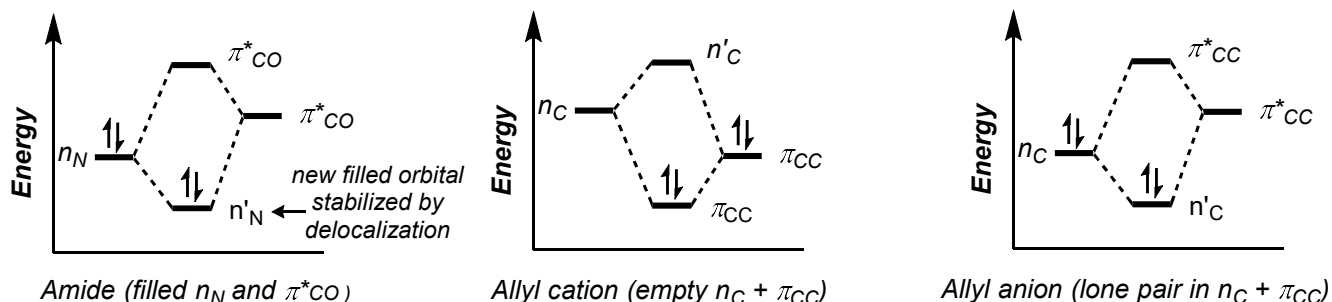
### Key Concept Review

#### Conjugation:

**Conjugated/delocalized  $\pi$  systems:** Due to their geometry, multiple adjacent parallel p orbitals and  $\pi$  bonds can combine to form extended (or delocalized) molecular orbitals. Frequently, we represent delocalization with resonance structures, but in order to understand its effects on the chemical and physical properties of molecules, it can be also be helpful to think of it in terms of orbitals. In order to facilitate the optimal orbital overlap necessary for delocalization, all p orbitals must be parallel; as such, all atoms in the  $\pi$  system must lie in a plane. Systems in which more than two p orbitals are appropriately aligned to interact are called conjugated systems. Some simple conjugated systems are shown below:



**Stabilization by delocalization:** Spreading electron density over more than two atomic orbitals to form delocalized systems is more stabilizing than keeping electron density isolated in a simple  $\pi$  bond. This concept can be justified by considering the effects of orbital mixing. A filled and an empty orbital with the geometries necessary for interaction can combine to form two new orbitals. This results in a net decrease in the energy level of the filled molecular orbital and a net increase in the energy level of the unfilled molecular orbital. Overall, this has a stabilizing effect. Consider the following diagrams showing the orbital mixing for the molecules above:



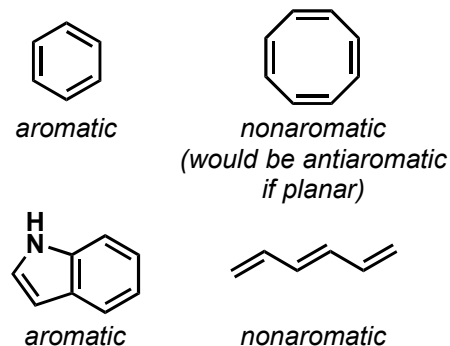
#### Aromaticity:

**Aromaticity:** Molecules with a *planar, cyclic, uninterrupted* conjugated  $\pi$  system containing  $4n + 2$  (i.e., 2, 6, 10,...) electrons are unusually stable (much more stable than their linear counterparts); this special stability is called "aromaticity," and molecules that possess it are called "aromatic" molecules or "arenes." Aromatic portions of a larger molecule are called "aryl groups".

**Antiaromaticity:** Conversely, molecules that contain a planar, cyclic, uninterrupted conjugated  $\pi$  system containing  $4n$  (i.e. 0, 4, 8, ...) electrons display exceptional instability called "antiaromaticity." This destabilization is so great that antiaromatic molecules cannot exist, because any molecule with  $4n$   $\pi$  electrons will *decompose or distort from planarity* in order to avoid conjugation.

**Nonaromaticity:** Molecules that lack a planar, cyclic, uninterrupted conjugated  $\pi$  system can be neither aromatic nor antiaromatic, and are called "nonaromatic." Nonaromatic molecules include (but are not limited to) molecules with:

- (1) non-cyclic  $\pi$  systems
- (2) a cyclic  $\pi$  system disrupted by one or more  $sp^3$ -hybridized atoms
- (3) non-planar  $\pi$  systems

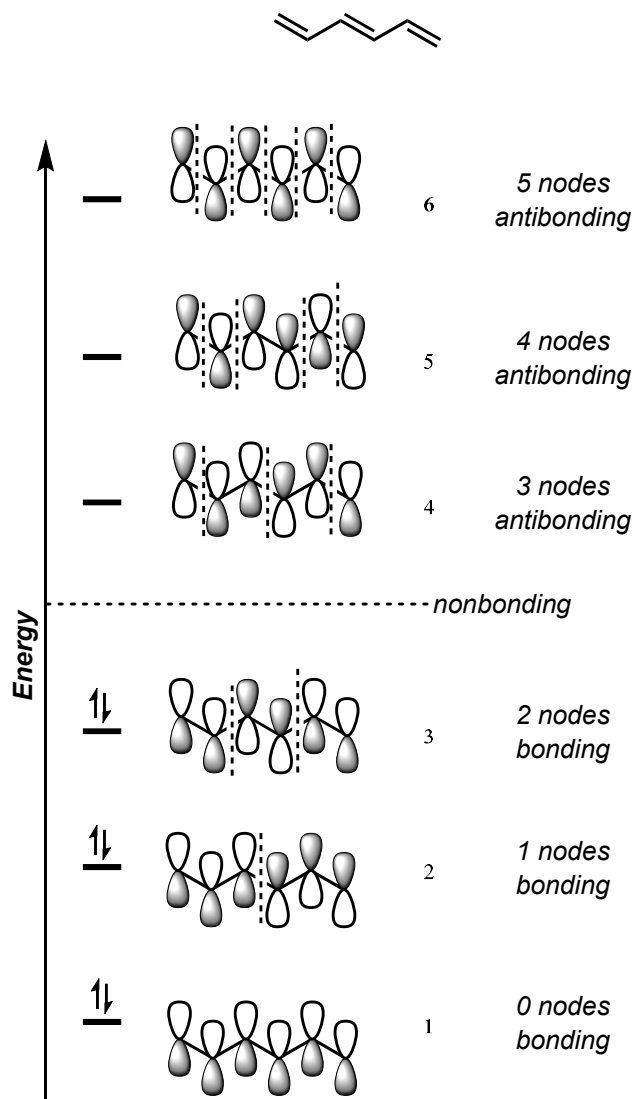


**Hückel MO Theory:** A mathematical theory used to predict the energy levels for the  $\pi$  system of a conjugated molecule by treating the system as a linear combination of atomic p orbitals (LCAO). A  $\pi$  system made from  $n$  p orbitals ( $n = \text{integer}$ ) must contain  $n$  molecular orbitals. A *node* represents a point at which there is a change in sign in the wavefunction (change in phasing of p orbitals) and *no probability of finding an electron*. The lowest energy orbital always has zero nodes, and the number of nodes increases in each energy level up to the highest energy orbitals, which in acyclic systems have  $(n - 1)$  nodes.

**Hückel MOs for linear  $\pi$  systems:** To build an MO diagram for the  $\pi$  system of a *linear* conjugated molecule:

- (1) Determine the number of atoms ( $n$ ) contributing p orbitals to the  $\pi$  system; there will be the same number of energy levels as there are p orbitals.
- (2) Draw  $n$  energy levels along a vertical energy scale.
- (3) Next to each energy level, sketch an array of  $n$  p orbitals.
- (4) At the lowest energy level, there will be 0 nodes; shade the orbitals to represent that they are all in-phase.
- (5) At the next energy level, there will be 1 node; draw this node in the molecule to split the  $\pi$  system as symmetrically as possible. Then, shade the orbitals to represent a single phase change at that node.
- (6) Moving up through the energy levels, repeat this analysis, adding 1 node at each level; these nodes should be placed to split the  $\pi$  system as symmetrically as possible. This can be often be done by eye. Alternatively, if we number the carbons from 1 to  $x$ , for each  $\Psi_i$  (MO) we have *sign inversions at every  $(x+1)/i$* .
- (7) Count the number of electrons in the  $\pi$  system, and fill them in from lowest energy to highest.
- (8) Any orbitals that fall exactly halfway up the energy scale will be nonbonding. Orbitals below the halfway point will all be bonding; orbitals above the halfway point will all be antibonding. This is most commonly seen when there are an odd number of p orbitals in the pi system.

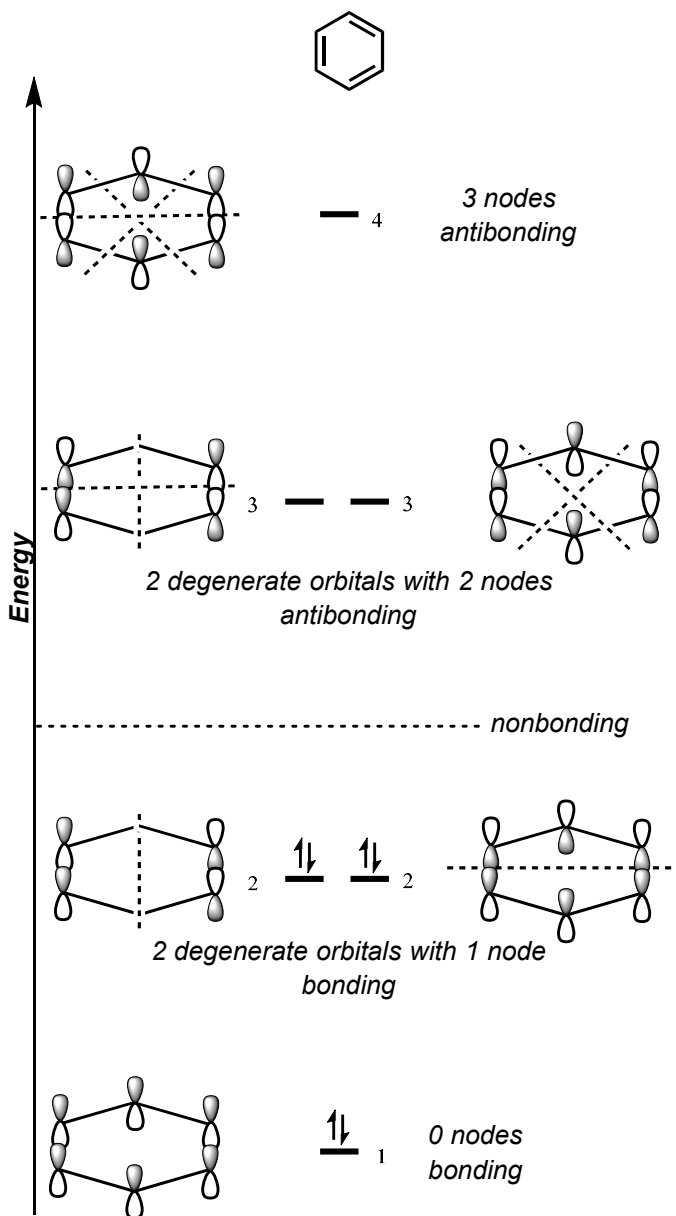
Hückel MO diagram for hexatriene:



**Frost circle mnemonic:** To quickly build a molecular orbital diagram for the  $\pi$  system of a *cyclic* conjugated molecule:

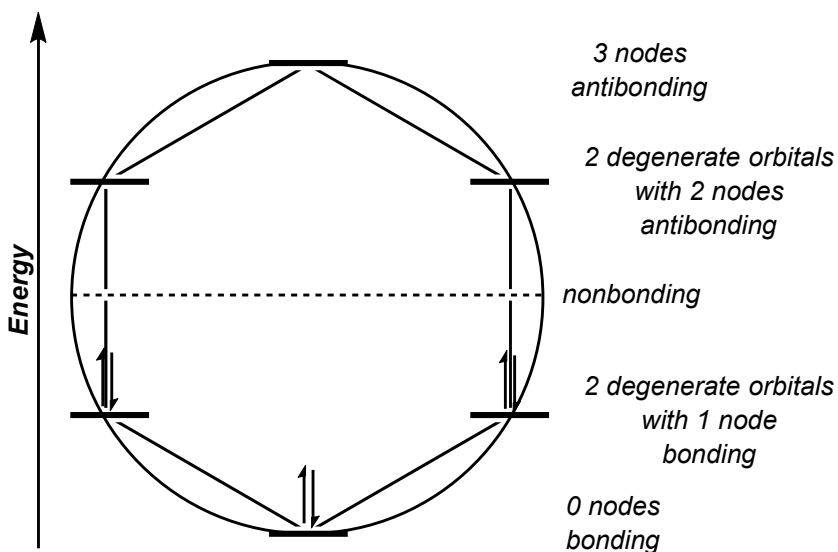
- (1) Determine the number of atoms ( $n$ ) in the ring contributing p orbitals to the  $\pi$  system.
- (2) On a vertical energy axis, inscribe a regular polygon with  $n$  points in a circle with one point down. There is a MO at the energy level corresponding to every point that the polygon touches the circle. Above the unique lowest MO, the MOs go up in pairs until reaching the highest energy MO (which is unique for even-numbered systems, and degenerate for odd-numbered systems).
- (3) Next to each orbital energy level, sketch  $n$  p orbitals superimposed on the cyclic framework.
- (4) At the lowest energy level, there will be 0 nodes; shade the orbitals to represent that they are all in-phase.
- (5) At the next energy level, there will be 2 degenerate orbitals, each with 1 node; draw the node in the molecule to split the  $\pi$  system symmetrically two different ways (one going through the bottom vertex, one  $90^\circ$  from this). Shade the orbitals to represent a single phase change at the node.
- (6) Moving up through the energy levels, repeat this analysis, adding 1 node at each level; these nodes should be placed to split the  $\pi$  system as symmetrically as possible.
- (7) Count the number of electrons in the  $\pi$  system, and fill them in from lowest in energy to highest.

Hückel MO diagram for benzene:



Frost circle for benzene:

Notice that by simply inscribing the regular polygon in a circle and following the Frost mnemonic, we are able to obtain the same qualitative information about the orbitals as in the full Hückel molecular orbital diagram. However, if we want to visualize the actual  $\pi$ -orbitals, we must construct the full diagram as done above.



## Workshop Problems

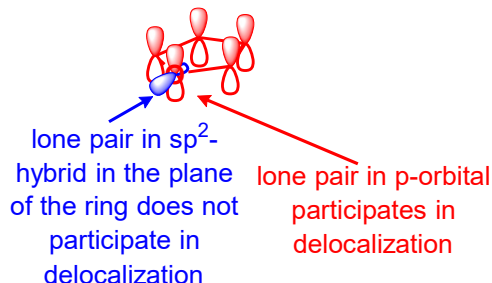
### Workshop Problem 1: Aromaticity

Using the Hückel definition of aromaticity, classify each of the following molecules as aromatic, antiaromatic, or nonaromatic. Then, indicate whether or not you would expect the ring in each molecule to assume a planar conformation. For 1a-1c, sketch the  $\pi$  system of the molecule to support your answer.

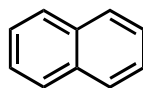
1-a.



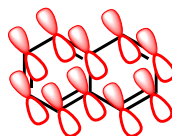
aromatic ( $6\pi$  electrons includes O lone pair), planar



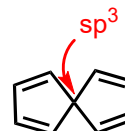
1-b.



aromatic,  $10\pi$  electrons, planar



1-c.

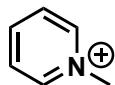


nonaromatic, not planar



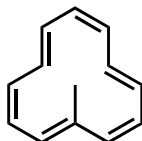
90 degree angle between the 2  $\pi$ -systems; no delocalization between them is possible

1-d.



aromatic ( $6\pi$  electrons) planar

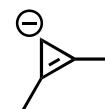
1-e.



nonaromatic ( $12\pi$  electrons) not planar

the methyl group prevents the structure from existing in a planar state

1-f.



nonaromatic (planar, but lone pair in  $sp^3$  orbital to avoid conjugation/anti-aromaticity)

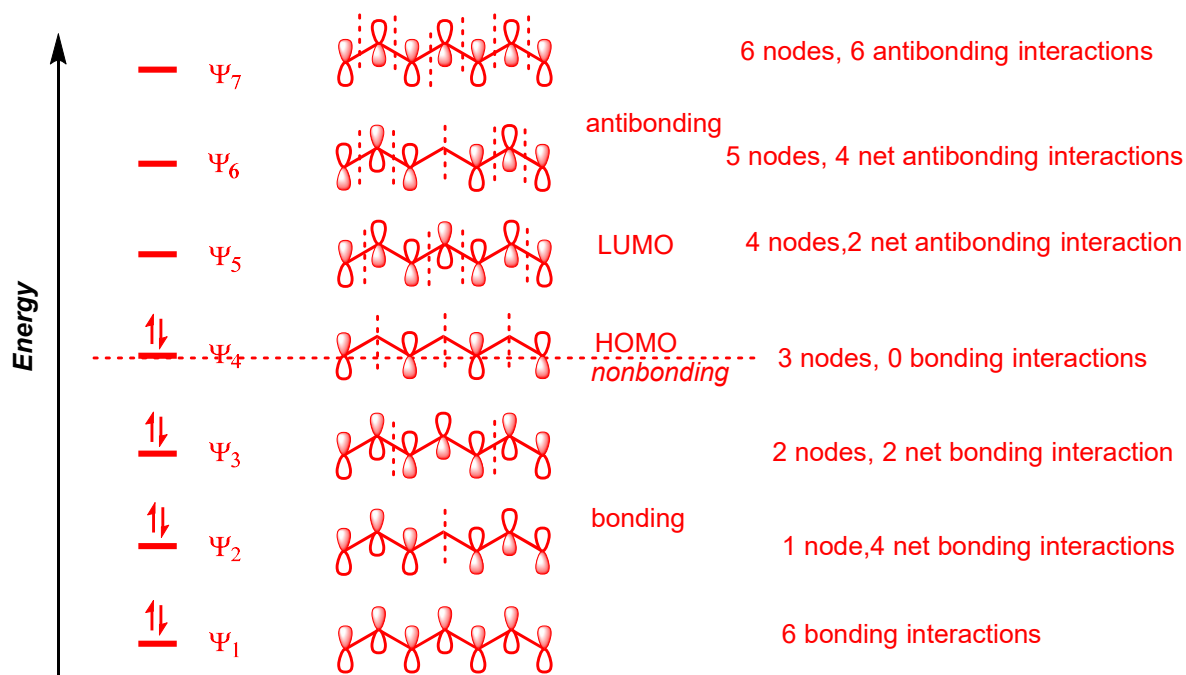
### Workshop Problem 2: Hückel MO Diagrams

Conjugated systems can be reactive at multiple sites. Here we will use Hückel MO theory to understand the basis for the typical pattern of reactivity.

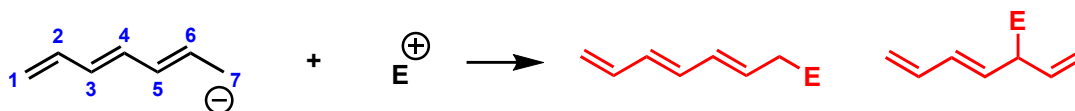
2-a. Provide clearly drawn line/skeletal structures of all important resonance forms of heptatrienyl anion (you do not need to include "no-bond" resonance structures). Use the arrow-pushing formalism to represent how the electron distribution changes between each resonance structure. Draw all lone pairs, and indicate formal charges where relevant.



**2-b.** On the axes below, construct a qualitative MO diagram for the  $\pi$ -system of heptatrienyl anion. Fill in the diagram with the appropriate number of electrons and identify the HOMO and LUMO. Then, sketch the molecular orbitals next to their corresponding energy levels. Do not worry about the orbital coefficient at each atom, but clearly show any nodes/phase changes.



**2-c.** Predict the potential product(s) of a reaction between heptatrienyl anion and a generic electrophile ( $E^+$ ). In two or three sentences, justify your prediction with your resonance structures from part **a** and with your molecular orbital diagram from part **b**.



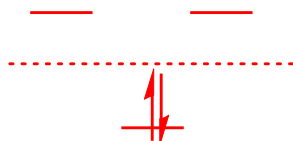
Both C1, C3, C5, and C7 have negative character (see the resonance structures in part a), rendering them nucleophilic at those sites. Furthermore, C1, C3, C5, and C7 have orbital character in the HOMO (the nucleophilic orbital). The presence of electron density at these sites in the HOMO causes these sites to be the most nucleophilic; reactions at C1 and C7 give the linear product while reactions at C3 and C5 give the branched product.

### Workshop Problem 3: Frost Circles

Frost circles are a helpful way to conceptualize the aromaticity of cyclic systems.

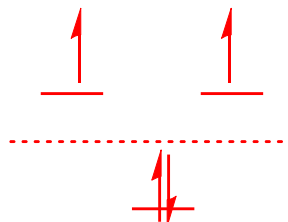
**3-a.** Draw the Frost Circles for the cyclopropenium cation and oxirene below. Comment on the aromaticity of each molecule.

cyclopropenium cation



aromatic

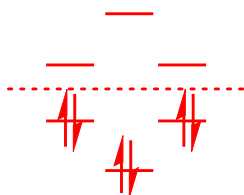
oxirene



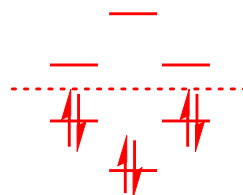
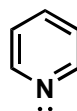
antiaromatic

**3-b.** Using Frost Circles, rationalize why benzene and pyridine (drawn below) are both aromatic despite the difference in their chemical formulae.

benzene



pyridine



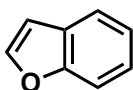
These compounds are both aromatic despite the difference in chemical formulae because the lone pair on the nitrogen atom in pyridine is in an  $sp^2$ -orbital orthogonal to the  $\pi$  system.

### Practice Problems

#### Skillbuilder Problem 1: Aromaticity

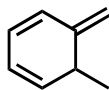
Using the Hückel definition of aromaticity, classify each of the following molecules as aromatic, antiaromatic, or nonaromatic. Then, indicate whether or not you would expect the ring in each molecule to assume a planar conformation.

1-a.



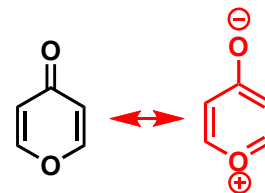
aromatic (10  $\pi$  electrons)  
planar, includes O lone pair

1-b.



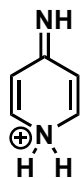
nonaromatic  
nonplanar

1-c.



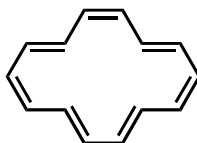
aromatic (6  $\pi$  electrons includes O lone pair in ring)  
planar

1-d.



nonaromatic  
nonplanar

1-e.



aromatic (14  $\pi$  electrons)  
planar

1-f.

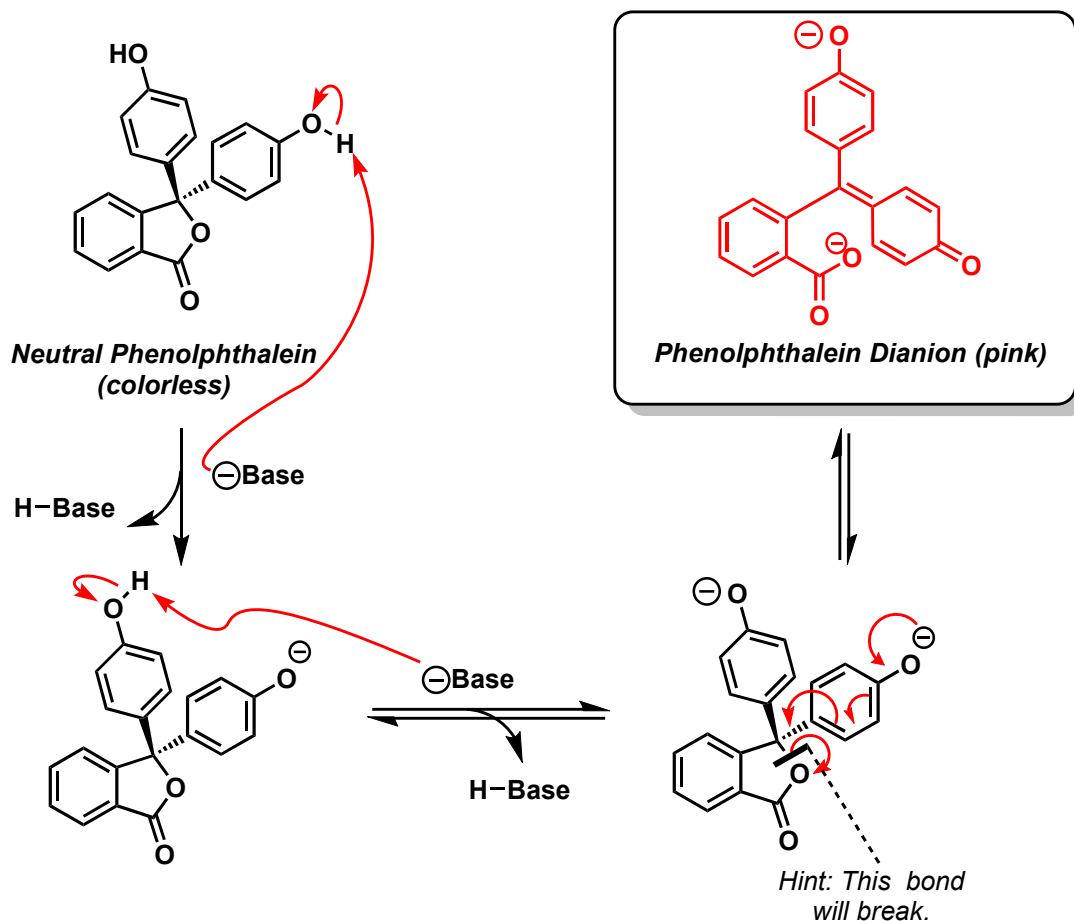


aromatic (6  $\pi$  electrons  
includes S lone pair)  
planar

### Skillbuilder Problem 2: Rationalizing Experimental Observations

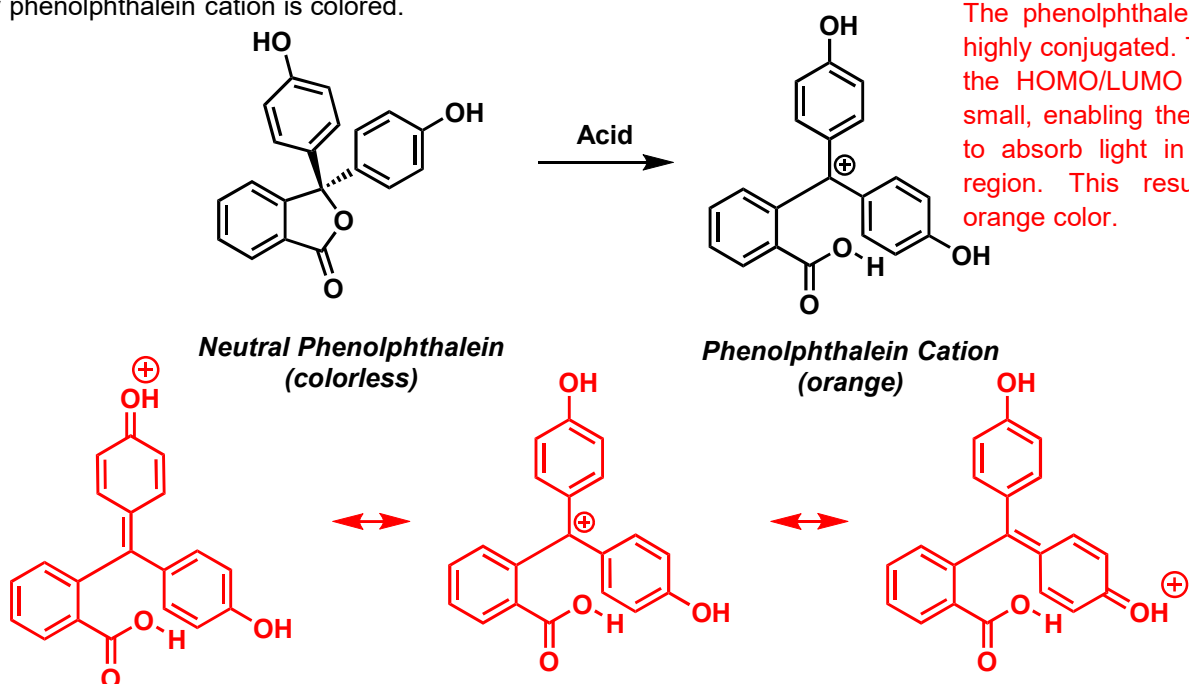
Phenolphthalein is a commonly used pH indicator. It is colorless in solution in its neutral form. However, under acidic or basic conditions, phenolphthalein becomes colored.

2-a. In presence of base, phenolphthalein becomes bright pink. Predict the structure of the colored product under basic conditions, and provide curly arrows to represent the redistribution of electrons in the mechanism for its formation. Briefly explain why phenolphthalein dianion is colored.

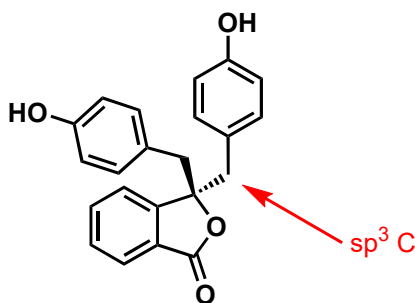


The phenolphthalein dianion (unlike neutral phenolphthalein) is highly conjugated. This causes the HOMO/LUMO gap to be small, enabling the compound to absorb light in the visible region. This results in the pink color.

**2-b.** In presence of acid, phenolphthalein becomes orange. Briefly explain, with words and resonance structures, why phenolphthalein cation is colored.

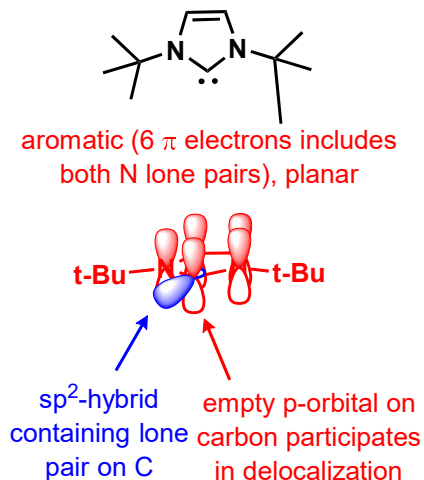


**2-c.** Would you expect the molecule below to become colored in basic medium? Justify your answer in one or two sentences.



No. The molecule cannot become highly conjugated upon deprotonation because an  $sp^3$  carbon disrupts the  $\pi$ -system.

**Challenge Problem 1.** The structure below is an N-heterocyclic carbene, and is aromatic. Explain why it is aromatic, by sketching the  $\pi$  system of the molecule. Note that the C atom bearing the lone pair does not have a formal charge!





## Challenge Problem 2

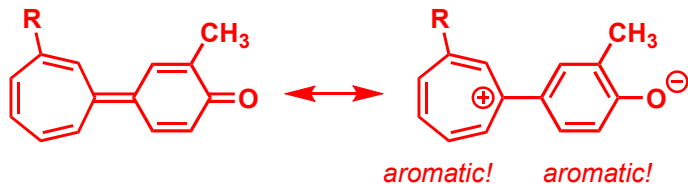
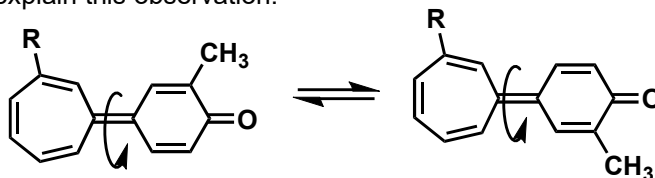
Using your understanding of delocalization and aromaticity, explain each of the following experimental observations.

**2-a.** 1,2-Dideuteriocyclobutadiene exists in two distinct rectangular (not square) forms. Please explain this observation.



If 1,2-dideuteriocyclobutadiene was square, it would have four electrons in the cyclic, conjugated array of p-orbitals, and would thus be antiaromatic. By distorting into a rectangle, the compound prevents conjugation of the two double bonds (by minimizing orbital overlap along the long sides of the rectangle) thereby avoiding the energetic penalty for antiaromaticity. Distortion in either direction makes different rectangular forms of 1,2-dideuteriocyclobutadiene, but both forms are equally capable of avoiding antiaromaticity and, therefore, both exist.

**2-b.** The barrier to rotation about a C=C bond is typically restricted, with an energetic barrier of ~60 kcal/mol. However, in the compound shown below, rotation about the C=C bond is unusually facile, with a 14 kcal/mol barrier to rotation. Please explain this observation.



The bond has substantial single bond character due to a very significant resonance structure in which both rings are aromatic. Single bonds have a very low barrier to rotation.